

Supplementary Information

Interfacing supramolecular and macromolecular chemistry: Metallo-supramolecular monomers incorporated into polymer networks

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Materials

All starting materials were purchased from Aldrich and BDH, methyl methacrylate (MMA) was filtered through basic alumina, other compounds were used without further purification.

Measurements

NMR spectra were recorded on Bruker DPX 300 and ACP 400 instruments using standard Bruker software. ESI mass spectra were recorded on a Micromass Quattro (II) (low resolution triple quadrupole mass spectrometer) at the EPSRC National Mass Spectrometry Service Center, Swansea. FAB mass spectra were recorded by the Warwick mass spectrometry service on a Micromass Autospec spectrometer using 3-nitrobenzyl alcohol as matrix. Microanalyses were conducted on a Leeman Labs CE44 CHN analyser by the University of Warwick Analytical service. Size exclusion chromatography (SEC) system equipped with a guard column, two 30 cm mixed D columns (Polymer Laboratories), and a differential refractive index on LC-1240 and UV-visible detectors on Shimadzu SPD-6AV, using tetrahydrofuran with toluene (as a flow rate marker) as eluent at 1 mL min⁻¹. The SEC was calibrated with 12 poly(MMA) standards in the range 6.85×10⁵ to 200 g.mol⁻¹.

Syntheses

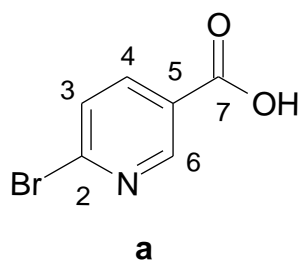
*6-bromonicotinic acid (a) adapted from literature*¹

2-bromo-5-methylpyridine (14.5 g, 0.084 mol) and Aliquat 336 (0.5 cm³) in distilled water (250 cm³) were heated to reflux. Potassium permanganate (37.8g, 0.239 mol) was added portionwise over 4.5 hours. Reflux was continued for 1 hour. The solution was filtered and the residue washed with hot water (100 cm³). The solution was then left open 2 days over which the remaining potassium permanganate had reduced to manganese dioxide. The brown solution was re-filtered and concentrated *in vacuo* to 100 cm³. The clear solution was acidified with 48% aqueous hydrobromic acid and placed in the fridge for 1 hour. Water (50 cm³) was then added and re-filtered. The filtrate was again concentrated *in vacuo* to 50 cm³ and further HBr added. This process was repeated once more. The product was dried under high vacuum to constant weight (8.7 g, 51%)

Positive ion Fast Atom Bombardment (FAB) : m/z 202 (M⁺, 20%), 120 (M⁺-Br, 100%)

¹H NMR (CDCl₃, 300 MHz, 298K) : δ 13.80 (1H, bs, OH), 8.85 (1H, d, *J*=2.6 Hz, H⁶), 8.17 (1H, dd, *J*=8.3, 2.6 Hz, H⁴), 7.82 (1H, d, *J*=8.3 Hz, H³) ppm

¹³C NMR (DMSO-d₆, 75.6 MHz, 298K) : δ 128.6 (C³), 140.3 (C⁴), 151.5 (C⁶), 127.1, 145.8 and 165.98 (C², C⁵ and C⁷) ppm



5-hydroxymethyl-2-bromopyridine (b) adapted from literature ²

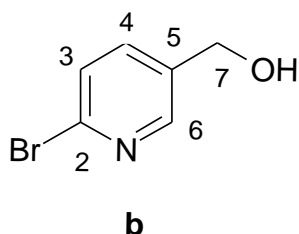
To an ice-cold slurry of **a** (7g, 35.65 mmol) in anhydrous THF (15 cm³) under dinitrogen was added borane THF complex (100 cm³ of 1 M in THF) over 15 min. The resulting yellow solution was stirred at room temperature for 3 hours. Saturated aqueous potassium carbonate was added until the mixture was just basic. Water (100 cm³) was added and the mixture extracted with ethyl acetate (3×100 cm³). The organic layers were combined, dried over sodium sulphate, filtered and evaporated to give an off white oil. The oil was subjected to flash chromatography on silica loaded in DCM and eluted with 2% methanol : DCM. Fractions with R_f=0.19 (TLC run with 2% methanol : DCM) were collected to yield a colourless oil which crystallised in air to a white solid (4.23g, 63%)

Positive ion EI : m/z 188 (M⁺-25%), 172 (M⁺-OH, 15%), 158 (M⁺-CH₂OH, 20%), 109 (M⁺-Br, 45%)

Microanalysis : found C, 38.6; H, 3.3; N, 7.1. Calculated from C₆H₆NOBr : C, 38.3; H, 3.2; N, 7.5%

¹H NMR (CDCl₃, 300 MHz, 298K): δ 8.23 (1H, d, J=2.1 Hz, H⁶), 7.59 (1H, dd, J=8.3, 2.5 Hz, H⁴), 7.45 (1H, d, J=8.3 Hz, H³), 4.83 (1H, bs, OH), 4.66 (2H, s, CH₂) ppm

¹³C NMR (CDCl₃, 75.6 MHz, 298K) : δ 148.9 (C⁶), 138.1 (C⁴), 128.4 (C³), 141.0 (C²), 136.5 (C⁵), 61.9 (C⁷) ppm



2-bromo-5-tert-butyldimethylsilyl-methylpyridine (c)

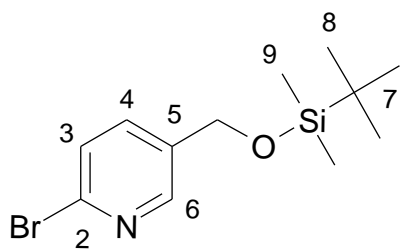
To a stirred solution of **b** (4.23 g, 0.022 mol) in dimethylformamide (22.5 cm³) and triethylamine (3.13 cm³) was added tert-butyldimethylsilyl chloride. The mixture was stirred at room temperature under dinitrogen for 1 hour and subsequently diluted with diethyl ether (200 cm³) and extracted with water (3×100 cm³). The ether layer was dried over sodium sulphate and evaporated to give a pale yellow oil. Column chromatography was performed on silica with DCM as eluent. The product was collected and evaporated to give a white oil (6.0 g, 88%) at R_f=0.4 with TLC run in DCM

Positive ion CI : m/z 303 (MH⁺, 62%), 246 (MH⁺-tBu, 32%), 224 (MH⁺-Br, 54%), 187 (MH⁺-SiMe₂-tBu, 61%), 172 (MH⁺-OSiMe₂-tBu, 100%)

Microanalysis : found : C, 47.5; H, 6.7; N, 4.7. Calculated for C₁₂H₂₀NOBrSi : C, 47.5; H, 6.7; N, 4.6%

¹H NMR (CDCl₃, 300 MHz, 298K) δ 8.29 (1H, d, J=1.7 Hz, H⁶), 7.51 (1H, dd, J=8.1, 2.3 Hz, H⁴), 7.43 (1H, d, J=8.1 Hz, H³), 4.68 (2H, s, CH₂), 0.94 (9H, s, Si-tBu), 0.12 (6H, s, Si-CH₃) ppm

^{13}C NMR (CDCl_3 , 75.5 MHz, 298K) : δ : 148.5 (C^6), 140.9 (C^5), 137.0 (C^4), 136.5 (C^2), 128.1 (C^3), 62.4 (CH_2), 26.2 (C^8), 18.7 (C^7), 4.9 (C^9) ppm



c

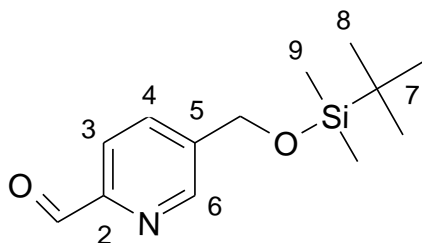
5-tert-butyl(dimethyl)silyl-pyridine-2-carboxaldehyde (d)

To a stirred solution of **c** (5.3 g, 0.018 mol) in anhydrous THF (30 cm^3) at -78°C under dinitrogen was added butyllithium (13 cm^3 of 1.6 M solution in hexane) over 15 min. The dark solution was stirred for a further 5 min. After stirring, DMF (1.62 cm^3) was added and the mixture stirred at -78°C for a further 5 min. After this time the flask was removed from the cold bath and then left to warm at room temperature. Water (1 cm^3) was added to quench the reaction and the mixture diluted with DCM (50 cm^3). The orange solution was filtered and subjected to flash chromatography on silica, eluted with DCM with TLC run with 5% methanol : DCM. Fractions containing product were collected at $R_f=0.65$ and collected to give a pale yellow oil (1.3g, 30%)

Positive ion CI : m/z 252 (MH^+ , 100%), 138 ($\text{MH}^+-\text{SiC}_6\text{H}_{13}$, 50%), 252 ($\text{MH}^+-\text{SiC}_6\text{H}_{13}$, 22%)

^1H NMR (CDCl_3 , 300 MHz, 298K) : 9.94 (1H, s, CHO), 8.61 (1H, s, H^6), 7.83 (1H, d, $J=7.9$ Hz, H^3), 7.72 (1H, d, $J=7.9$ Hz, H^4), 4.73 (2H, s, CH_2), 0.82 (9H, s, tBu), 0.01 (6H, s, CH_3) ppm

^{13}C NMR (CDCl_3 , 75.5 MHz, 298K) : 194.0 (CHO), 152.2 (C^2), 148.5 (C^6), 142.2 (C^5), 134.9 (C^4), 121.9 (C^3), 62.8 (CH_2), 26.2 (C^8), 18.7 (C^7), 5.0 (C^9) ppm



d

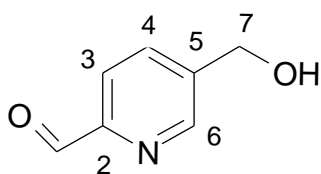
5-hydroxymethyl-pyridine-2-carboxaldehyde (e)

To a stirred solution of **d** (1.3 g, 5.17 mmol) in THF (11.5 cm^3) in an open flask at 0°C was added tetrabutylammonium fluoride 1M in THF (5.17 cm^3 , 5.17 mmol) over 2 min. The orange mixture was stirred for a further 30 min before the addition of a few drops of water and 2% methanol : DCM followed by 3 % methanol : DCM. The product was collected at $R_f = 0.3$ and evaporated to a pale yellow oil (0.39 g, 55%) TLC performed in 10% methanol : DCM

Positive-ion EI : m/z 137 (M^+ , 100%)

^1H NMR (CDCl_3 , 300 MHz, 298K) : δ 10.05 (1H, s, CHO), 8.75 (1H, bs, H^6), 7.94 (1H, d, $J=7.9$ Hz, H^3), 7.88 (1H, dd, $J=7.9, 1.8$ Hz, H^4), 4.85 (2H, s, CH_2) ppm

^{13}C NMR (CDCl_3 , 400 MHz, 298K) : δ 193 (CHO), 152.4 (C^2), 149.0 (C^6), 141.6 (C^5), 135.8 (C^4), 122.2 (C^3), 62.6 (C^7) ppm



e

Functionalisations

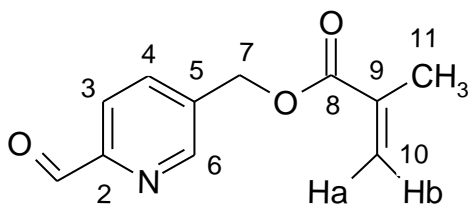
5-(methacryloyl) methyl pyridine-2-carboxaldehyde:

e (0.39 g, 2.85 mmol) was dissolved in THF (25 cm³) and cooled in an ice bath. Triethylamine (0.6 cm³, 4.28 mmol) and methacryloyl chloride (0.28 cm³, 2.85 mmol) were dissolved in THF (15 cm³) and also cooled. The 5-(hydroxymethyl)-pyridine-2-carboxaldehyde and triethylamine solution was then added dropwise to the second solution. The resulting solution was left stirring open to air at room temperature for 18 hours. A white precipitate was removed by filtration and washed with THF (5 cm³). The resulting filtrate was evaporated *in vacuo* to a yellow oil. Chloroform (200 cm³) was added and extracted with aqueous sodium carbonate (200 cm³) the organic layer was then collected, dried over sodium sulphate and again evaporated *in vacuo*. The resulting yellow oil was subjected to column chromatography on silica, loaded in DCM and eluted with 2% methanol : DCM solution. TLC run in 10% methanol : DCM. The pale yellow product was collected at R_f=0.4 (0.18 g, 30%)

Positive-ion EI : m/z 205 (M⁺, 28%), 188 (M⁺-OH, 29%), 177 (MH⁺-CHO, 40%), 120 (M⁺-C₄H₅O₂, 34%)

¹H NMR (CDCl₃, 400 MHz, 298K) : δ 10.17 (1H, s, CHO), 8.83 (1H, s, H⁶), 7.93 (1H, dd, J=7.8 Hz, H³), 7.93 (1H, dd, J=7.8, 1.5 Hz, H⁴), 6.21 (1H, m, H^{a/b}), 5.68 (1H, m, H^{a/b}), 5.33 (2H, s, CH₂), 2.01 (3H, s, CH₃) ppm

¹³C NMR (CDCl₃, 100.6 MHz, 298K) : δ 193.0 (CHO), 167.2 (C^{2/5/9}), 152.9 (C^{2/5/9}), 149.9 (C⁶), 136.9 (C⁴), 136.1 (C^{2/5/9}), 127.1 (C¹⁰), 121.9 (C³), 64.3 (CH₂), 18.7 (CH₃) ppm.



1

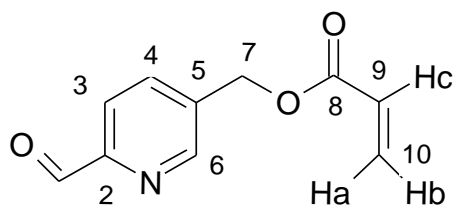
5-(acryloyl) methyl pyridine-2-carboxaldehyde:

The experimental protocol is similar to the synthesis of **1** except that acryloyl chloride is used instead of methacryloyl chloride. The product was collected at R_f=0.7. TLC run in 10% methanol : DCM (0.23 g, 31%)

Mass spectrum +ve EI : m/z 191 (M⁺, 25%), 163 (M⁺-CO, 100%), 136 (M⁺-C₃H₃O, 23%), 120 (M⁺-C₃H₃O₂, 15%), 109 (M⁺-C₄H₃O₂, 40%), 92 (M⁺-C₄H₃O₃, 45%)

¹H NMR (CDCl₃, 300 MHz, 298K) : δ 10.02 (1H, s, CHO), 8.77 (1H, d, J=1.3 Hz, H⁶), 7.95 (1H, d, J=7.9 Hz, H³), 7.87 (1H, dd, J=8.1, 1.9 Hz, H⁴), 6.46 (1H, dd, J=17.3, 1.3 Hz, H^b), 6.16 (1H, dd, J=17.3, 10.4 Hz, H^c), 5.90 (1H, dd, J=10.4, 1.3 Hz, H^a), 5.28 (2H, s, CH₂) ppm

^{13}C NMR (CDCl_3 , 75.6 MHz, 298K) : 196.0 (CHO), 166.0 (C^8), 152.9 (C^2), 150.1 (C^6), 137.0 (C^4), 132.5 (C^9), 128.0 (C^{10}), 121.9 (C^3), 64.5 (C^7) ppm



2

Preparation of Ligands

L¹:

1 (0.16g, 0.80 mmol) was dissolved in ethanol (25 cm³) and added dropwise to a solution of 4,4'-methylene dianiline (0.079 g, 0.40 mmol) also in ethanol (25 cm³). The reaction mixture was left stirring at room temperature for 19 hours after which time a pale yellow precipitate was collected by vacuum filtration (0.18 g, 37 %)

Positive ion FAB : m/z 573 (MH^+ , 100%), 503 ($\text{M}^+ - \text{C}_4\text{H}_5\text{O}$, 10%)

Microanalysis : found : C, 72.6; H, 5.6; N, 9.6; calculated for $3(\text{C}_{35}\text{H}_{32}\text{NO}_4) \cdot \text{H}_2\text{O}$: C, 72.6; H, 5.7; N, 9.7%

^1H NMR ($\text{DMSO}-d_6$, 300 MHz, 298K) : δ 8.75 (2H, s, H^i), 8.61 (2H, s, H^6), 8.18 (2H, d, $J=8.2$ Hz, H^4), 7.98 (2H, d, $J=8.6$ Hz, H^3), 7.33 (8H, s, H^{ph}), 6.12 (2H, s, $\text{H}^{\text{a/b}}$), 5.75 (2H, s, $\text{H}^{\text{a/b}}$), 5.30 (4H, s, CH_2), 4.03 (4H, s, H^{sp}), 1.92 (6H, s, CH_3) ppm

L²:

The experimental protocol is similar to **L¹** except that **2** (0.22g, 1.18 mmol) is used instead of **1** with 4,4'-methylene dianiline (0.12 g, 0.60 mmol). The product is collected by vacuum filtration (0.14g, 42%)

Positive-ion EI : m/z 544 (M^+ , 100%), 473 ($\text{M}^+ - \text{C}_3\text{H}_3\text{O}_2$, 22%), 402 ($\text{M}^+ - \text{C}_6\text{H}_6\text{O}_4$, 15%)

^1H NMR (CDCl_3 , 300 MHz, 298K) : δ 8.74 (2H, d, 1.5 Hz, H^6), 8.65 (2H, s, H^i), 8.25 (2H, d, $J=8.1$ Hz, H^3), 7.86 (2H, dd, $J=8.1, 1.9$ Hz, H^4), 7.29 (8H, s, H^{ph}), 6.50 (2H, dd, $J=17.3, 1.3$ Hz, H^b), 6.20 (2H, dd, $J=17.3, 10.4$ Hz, H^c), 5.90 (2H, dd, $J=10.4, 1.3$ Hz, H^a), 5.31 (4H, s, CH_2), 4.07 (2H, s, H^{sp}) ppm

^{13}C NMR (CDCl_3 , 75.6 MHz, 298K) : δ 167.0 (C^8), 159.9 (C^i), 155.0 ($\text{C}^{2,5,11,14}$), 149.8 (C^6), 149.3 ($\text{C}^{2,5,11,14}$), 140.3 ($\text{C}^{2,5,11,14}$), 137.0 (C^4), 133.4 ($\text{C}^{2,5,11,14}$), 132.2 (C^{10}), 130.2 (C^{ph}), 128.2 (C^9), 122.0 ($\text{C}^{3,\text{ph}}$), 121.8 ($\text{C}^{3,\text{ph}}$), 63.9 (C^7), 41.5 (C^{sp}) ppm

Preparation of the Supramolecular Comonomers **C^{1,2}**

C¹: $[\text{Fe}_2\text{L}^1_3][\text{PF}_6]_4$

L¹ (0.030 g, 0.052 mmol) and iron(II) chloride (0.007 g, 0.035 mmol) were heated under reflux in methanol for 24 hours. Methanolic ammonium hexafluorophosphate was then added to the purple solution. Diethyl ether (5 cm³) was added and a deep purple precipitate was recovered by vacuum filtration. Yield (0.022 g, 52%)

Positive-ion FAB: m/z 2264 ($[\text{Fe}_2(\text{L}^2)_3(\text{PF}_6)_3]^+$), 2196 ($[\text{Fe}_2(\text{L}^2)_3(\text{PF}_6)_3]^+-\text{C}_4\text{H}_5\text{O}$), 2138 ($[\text{Fe}_2(\text{L}^2)_3(\text{PF}_6)_3(\text{F}^-)]^+$), 2119 ($[\text{Fe}_2(\text{L}^2)_3(\text{PF}_6)_2]^+$), 2097 ($[\text{Fe}_2(\text{L}^2)_3(\text{PF}_6)_3]^+-\text{C}_4\text{H}_5\text{O}$ and $\text{C}_5\text{H}_7\text{O}$), 2067 ($[\text{Fe}_2(\text{L}^2)_3(\text{PF}_6)_2(\text{F}^-)]^+-\text{C}_4\text{H}_5\text{O}$), 2051 ($[\text{Fe}_2(\text{L}^2)_3(\text{PF}_6)_2]^+-\text{C}_4\text{H}_5\text{O}$), 1993 ($[\text{Fe}_2(\text{L}^2)_3(\text{PF}_6)(\text{F}^-)]^+$), 1974 ($[\text{Fe}_2(\text{L}^2)_3(\text{PF}_6)]^+$), 1925 ($[\text{Fe}_2(\text{L}^2)_3(\text{PF}_6)(\text{F}^-)]^+-\text{C}_4\text{H}_5\text{O}$), 1906 ($[\text{Fe}_2(\text{L}^2)_3(\text{PF}_6)]^+-\text{C}_4\text{H}_5\text{O}$)

Microanalysis: found C, 50.9; H, 3.9; N, 6.7. Calculated for $[\text{Fe}_2(\text{C}_{35}\text{H}_{32}\text{N}_2\text{O}_4)_3][(\text{PF}_6)_4] \cdot 3(\text{H}_2\text{O})$: C, 51.2; H, 4.2; N, 6.8%

^1H NMR (CD_3CN , 300 MHz, 298K): δ 8.91 (6H, s, H^i), 8.55 (6H, d, $J=8.1$ Hz, H^4), 8.36 (6H, d, $J=7.9$ Hz, H^3), 7.30 (6H, s, H^6), 6.93 (12H, bs, H^{ph}), 5.99 (6H, s, H^{ab}), 5.71 (6H, s, H^{ab}), 5.50 (12H, bs, H^{ph}), 5.27 (12H, s, CH_2), 4.02 (6H, s, H^{sp}), 1.88 (18H, s, CH_3) ppm

C²: $[\text{Fe}_2\text{L}^2_3][\text{PF}_6]_4$

Same protocol as used for **C¹** except that **L²** (0.030 g, 0.06 mmol) and iron(II) chloride (0.007 g, 0.035 mmol) were heated under reflux in methanol for 20 hours. Yield (0.026 g, 60%)

Positive-ion ESI: m/z 1018 ($[\text{Fe}_2(\text{L}^3)_3(\text{PF}_6)_2]^{2+}$), 991 ($[\text{Fe}_2(\text{L}^3)_3(\text{PF}_6)_2]^{2+}-\text{C}_3\text{H}_3\text{O}$), 630 ($[\text{Fe}_2(\text{L}^3)_3(\text{PF}_6)^{3+}$), 612 ($[\text{Fe}_2(\text{L}^3)_3(\text{PF}_6)^{3+}-\text{C}_3\text{H}_3\text{O}$), 594 ($[\text{Fe}_2(\text{L}^3)_3(\text{PF}_6)^{3+}-2(\text{C}_3\text{H}_3\text{O})$), 436 ($[\text{Fe}_2(\text{L}^3)_3]^{4+}$), 423 ($[\text{Fe}_2(\text{L}^3)_3]^{4+}-\text{C}_3\text{H}_3\text{O}$), 409 ($[\text{Fe}_2(\text{L}^3)_3]^{4+}-2(\text{C}_3\text{H}_3\text{O})$)

Negative-ion ESI: m/z 145 (PF_6^-)

Microanalysis: found: C, 51.8; H, 3.8; N, 7.4. Calculated for $[\text{Fe}_2(\text{C}_{33}\text{H}_{28}\text{N}_2\text{O}_4)_3][\text{PF}_6]_4 \cdot (\text{CH}_3\text{CN})$: C, 51.3; H, 3.7; N, 7.7%

^1H NMR (CD_3CN , 300 MHz, 298K): δ 8.92 (6H, s, H^i), 8.54 (6H, d, $J=7.9$ Hz, $\text{H}^{3/4}$), 8.36 (6H, d, $J=7.5$ Hz, $\text{H}^{3/4}$), 7.25 (6H, s, H^6), 6.95 (12H, bs, H^{ph}), 6.40 (6H, d, $J=16.7$, H^b), 6.15 (6H, dd, $J=16.9$, 10.5 Hz, H^c), 6.00 (6H, d, $J=10.5$ Hz, H^a), 5.54 (12H, bs, H^{ph}), 5.28 (12H, s, CH_2), 4.03 (6H, s, H^{sp}) ppm

Random Copolymerisation Experiments

P¹:

C¹ (0.015 g, 0.006 mmol) and MMA (2 cm³, 19.07 mmol) were placed in a schlenk tube with a suba seal stopper. Nitromethane (4 cm³), AIBN (0.04 g, 0.24 mmol) were added under a blanket of dinitrogen. The tube was sealed and heated to 75°C for 36 hours. The copolymer is recovered at complete conversion by precipitation in hexane to give a purple solid (1.5g)

SEC: PDI (2.3), Mn (7800), Mw (18000)

^1H NMR (Water suppression, DMSO, 300 MHz, 298K): δ 4.42 (xH, bs, x CH_3NO_2), 3.57 (3nH, bs, polyOCH₃), 1.84 (2nH, bm, polyCH₂), 0.85 (3nH, bs, polyCH₃) ppm.

P²:

Same protocol used as **P¹** with these quantities **C²** (0.008 g, 0.003 mmol) and MMA (0.8 cm³, 7.99 mmol). The copolymer is recovered as a purple solid (0.4 g)

SEC: PDI (2.29), Mn (8300), Mw (19000)

^1H NMR (water suppression, CD_3CN , 300 MHz, 298K): δ 4.30 (xH, bs, x CH_3NO_2), 3.60 (3nH, bs, polyOCH₃), 2.15 (2nH, bm, polyCH₂), 0.82 (3nH, bs, polyCH₃) ppm

Extraction of the iron(II) from P²

The removal of the iron (II) from the purple copolymer P² was achieved by first forming a salt of EDTA following this procedure: *tetra* n-butyl ammonium salt was prepared by reacting EDTA with a solution of *tetra* n-butyl ammonium hydroxide in methanol and concentration *in vacuo* followed by drying under high vacuum to an off white crystalline solid. The EDTA salt was then dissolved in 5% methanol:dichloromethane and added to a solution of the copolymer also in 5% methanol:dichloromethane. After stirring the solution was extracted with water and the organic layer concentrated to give a white solid.

References

¹ Windschief P.M. and Vögtle F., *Synthesis*, **1994**, 87-92

² Ellingboe J. W., Antane M., Nguyen T. T., Collini M. D., Anyane S., Bender R., D. Hartupee D., White V., McCallum J., Hyung Park C., Russo A., Osler M. B., A. Wojdan A., Dinish J., Ho D. M. and Bagli J. F., *J. Med. Chem.*, **1994**, 37, 542